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This technical report has been reviewed and is approved for publication.

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A thorough study was conducted on the effect of thermal aging on graphite fibers. Thermal-oxidative properties were evaluated on available fibers at several temperature ranges. Activation energies were analytically determined from rates of isothermal weight loss. Sodium content was shown to lower activation energy and increase rate of oxidation.

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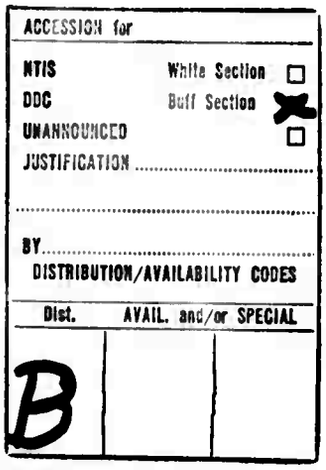
FOREWORD

The work reported here was performed in the Composite and Fibrous Materials Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio under Project 2419, Job Order No. 24190204, George Archibald, AFML/MBC, was the principal investigator.

This report was released by the author in December 1976, and covers the time period of April 1976 to June 1976.

The author wishes to acknowledge George Husman and Charles Browning in analyses and consultation of this report. The author would also like to thank Tim Hartness, University of Dayton Research Institute for invaluable assistance.



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SECTION I

INTRODUCTION

The use of graphite fiber reinforced composites for aerospace and commercial applications is widespread and is rapidly increasing. Previously unexplored areas for the application of high-temperature composites are now being explored. The introduction of processible thermally stable polyimide resins permits increased applications for composites in high-temperature areas. However, it is important that we understand the limitations of these graphite-reinforced composites.

One important area of concern is the thermal-oxidative stability of graphite fibers. Because there are many different forms of graphite fiber available, it is important to define the use temperature ranges for various fibers where they will exhibit optimum performance of oxidative degradation. The area of the interaction between the fiber and the resin matrix was not explored here, but will be covered in future work.

SECTION II

EVALUATION PROCEDURE

Isothermal weight loss (ITWL) is an important criteria for defining optimum use temperatures. The test procedure used herein involved placing fiber specimens in an isothermal air-circulating oven, removing them at periodic intervals, and weighing them to determine their ITWL. Thermal aging durations (at various temperatures) of up to 1000 hours were performed.

An elemental analysis was run on all available fibers before thermal aging. These data were compared with ITWL data to relate weightless behavior to the presence of trace metals.

Calculations were made to determine activation energies of some of the fibers. The effects of impurities on activation energy were then examined. These series of tests were run on all the samples available at the time, including the following fibers (lot number in parentheses):

Hercules HT-S (66-7, 54-4, 56-4, 1-45/83C)

Hercules HM-S

Hercules A-S

Modmor Type II

Union Carbide T-300/Union Carbide T-300 HP

Great Lakes CG-3

Celanese Celion

Several different batches of HT-S fiber were evaluated due to the wide variation in properties between batches.

1. WEIGHT LOSS

Available fibers were thermally aged at 450^{o}F, 500^{o}F, 550^{o}F, and 600^{o}F for intervals of 1000 hours. Fibers were also aged at 700^{o}F and

800°F for varying intervals depending on their thermal-oxidative stability. The results of these tests are summarized in Tables 1, 2, 3, 4, 5, and 6. These tables indicate there is a wide range in the thermal oxidative stability of the different fibers.

In several of the tables more than one batch of Hercules' HT-S is listed. This is due to the variation between certain batches. Batch 54-4 had very poor thermal-oxidative stability, while older batches and the most recent 56-4, performed significantly better.

The oxidative nature of graphite fiber degradation has been demonstrated in other studies (Reference 1) and will not be examined here.

When the extent of oxidation became high (in excess 50% weight loss) the effects became visually apparent.

Figure 1 illustrates the extent of thermal degradation of A-S fiber, as compared to HM-S fiber under the same conditions. At lower weight loss levels, there were no readily observable physical changes.

2. ELEMENTAL ANALYSIS

An elemental analysis was run on all the samples available. The samples contained mostly carbon with small amounts of nitrogen, oxygen, and hydrogen. An analysis was also run on trace metals. The element sodium was present in the largest amount in every sample. Figure 3 is a comparison of ITWL at given conditions (50 hours, 700°F) versus the respective fiber's sodium content. This graph illustrates the relationship between thermal-oxidative stability and sodium content. Table 7 lists the respective fibers and their sodium content.

TABLE 1

FIBER WEIGHT LOSS IN AIR 800°F

Fiber	PERCENT WEIGHT LOSS 3 Hours	5 Hours	10 Hours	20 Hours	50 Hours	200 Hours
A-S	11.71	22.1	45.7	92.9	100	
T-300	2.39	6.55	32.8	88.7	100	
MOD MOR II	5.00	7.29	14.4	24.9	51.3	
HT-S (0)	1.802	2.65	3.94	5.74	21.0	
HTS (N)	7.45	17.0	54.0	86.0	100	
HM-S	.600	.867	1.38	2.32	7.03	30.6
CG-3	50.9	82.0	100			
CG-5	.176	.266	.417	.683	1.70	7.16
HTS (66-7)	6.73	11.4	21.6	39.8	98.2	

0 - Old Fiber (Batch 1-45/83C)

N - New Fiber (Batch 54-4)

TABLE 2

FIBER WEIGHT LOSS IN AIR 700°F

Fiber	PERCENT WEIGHT LOSS 10 Hours	20 Hours	50 Hours	100 Hours	200 Hours	300 Hours
A-S	2.00	6.45	35.1	100	-	-
T-300	1.39	4.75	27.4	99.5	-	-
MOD MOR II	.950	1.96	4.18	6.57	9.20	12.7
HT-S (0)	.520	.710	1.03	1.62	2.65	5.3
HTS (N)	16.9	39.4	70.6	99.0		
HM-S	.256	.310	.434	.597	.879	1.27
CG-3	47.5	88.1	100			
CG-5	.192	.220	.358	.561	.852	1.25
HTS (56-4)	.100	.250	.310	.600	1.12	2.23
HTS (66-7)	3.00	5.00	11.4	15.0	19.5	24.0
C LION	1.2	2.0	4.1	12.9	15.2	30.0

0 - Old Fiber (Batch 1-45/83C)

N - New Fiber (Batch 54-4)

TABLE 3

FIBER WEIGHT LOSS IN AIR 600°F

Fiber	PERCENT WEIGHT LOSS 200 Hours	400 Hours	600 Hours	800 Hours	1000 Hours
A-S	2.45	12.9	36.5	74.0	95.1
T-300	3.47	8.1	28.2	40.5	57.0
MOD MOR II	.749	.895	1.10	1.40	1.50
HT-S (O)	.508	.593	.861	.960	1.26
HTS (O)	.34	.42	.65	.80	.96
HTS (N)	21.9	37.0	49.2	54.5	59.7
HM-S	.674	.437	.492	.615	.528
T-300 HP	2.13	6.80	12.62	22.19	24.64
CG-5	.28	.37	.46	.52	.59
Celion 6000	1.77	3.04	4.64	10.26	13.58

O - Old Fiber (Batch 1-45/83C)

N - New Fiber (Batch 54-4)

TABLE 4

FIBER WEIGHT LOSS IN AIR 550°F

Fiber	PERCENT WEIGHT LOSS 200 Hours	400 Hours	600 Hours	800 Hours	1000 Hours
A-S	.865	5.93	11.1	14.7	21.1
T-300	1.12	5.56	12.2	15.5	20.6
MOD MOR II	.682	.774	1.04	1.22	1.34
HT-S (O)	.682	.816	.980	1.11	1.16
HM-S	.464	.589	.605	.684	.723

O - Old Fiber (Batch 1-45/83C)

N - New Fiber

TABLE 5

FIBER WEIGHT LOSS IN AIR 500°F

Fiber	PERCENT WEIGHT LOSS 200 Hours	400 Hours	600 Hours	800 Hours	1000 Hours
A-S	.105	.715	1.63	2.20	.376
T-300	.450	.650	1.08	1.27	1.46
MOD MOR II	.480	.485	.525	.575	.642
HTS (0)	.470	.450	.520	.580	.673
HM-S	.305	.352	.610	.785	.970

0 - Old Fiber (Batch 1-45/83C)

N - New Fiber

TABLE 6

FIBER WEIGHT LOSS IN AIR 450°F

(+) Indicates Weight Gain

Fiber	PERCENT WEIGHT LOSS 200 Hours	400 Hours	600 Hours	800 Hours	1000 Hours
A-S	+.110	+.250	+.475	+.505	+.760
T-300	.340	.412	.750	1.37	.705
MOD MOR II	.385	.400	.405	.235	.566
HT-S (0)	.102	.175	.134	.170*	.197
HM-S	.305	.362	.560	.605	.618

0 - Old Fiber (Batch 1-45/83C)

N - New Fiber

Table 7

SODIUM CONTENT OF FIBERS

Fiber Grade	Sodium Content (Parts per Million)
CG-5	50
HM-S	100
HTS(0)*	100
T-300	200
T-300 HP	70
MM II	200
A-S	200
HTS-(N)**	1000
CG-3	2000
Celion 6000	80

* - (0) - (1-4 5/836)

** (N) - (54-4)

3. ACTIVATION ENERGY

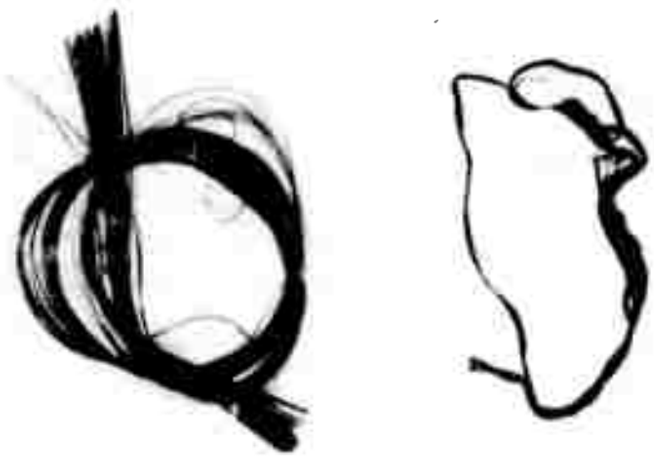
An analysis was made of the activation energies of the various fibers. The activation energy was determined from the Arrhenius equation (Reference 2):

$$\log K = \frac{E}{2.303RT}$$

where:

E = activation energy
K = specific reaction rate
R = universal gas constant
T = absolute temperature in Kelvin

The rate of ITWL with respect to time was used as the specific reaction rate. Only simple linear values for K were used. Nonlinear values for ITWL rate indicated a complex reaction mechanism. This report will attempt to develop a simple model for fiber thermal oxidative degradation. For all samples evaluated, an initial interval was disregarded. This was done to permit the curve to stabilize at a linear rate. This initial variation was attributed to surface impurities. Once these impurities were burned off, several of the fibers oxidized at a linear rate.



Left; HM-S
(1000 hours, 600°F)

Right; A-S
(1000 hours, 600°F)

Figure 1. Thermally Aged Fibers

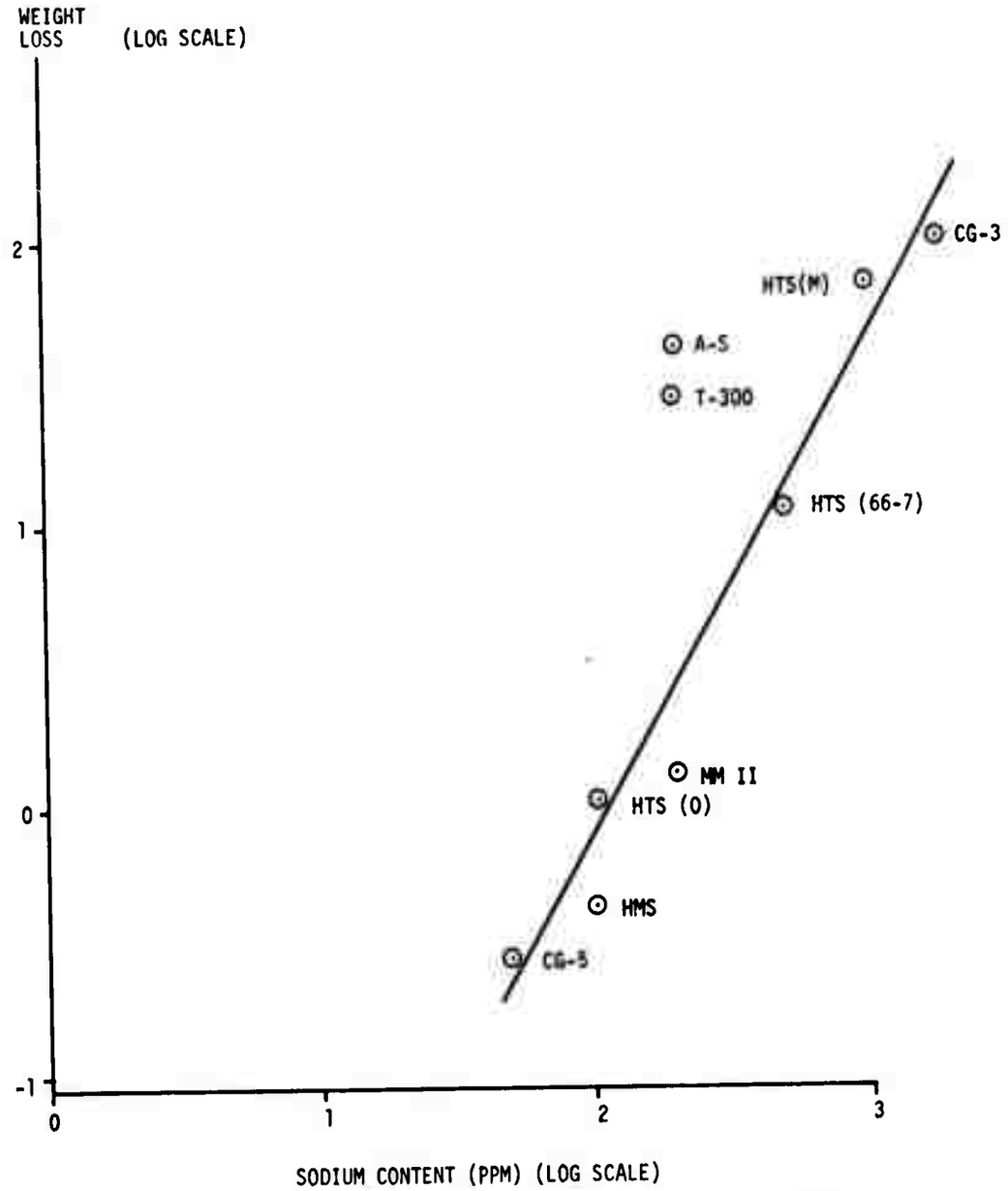


Figure 2. Log of Sodium Content vs. Log of Weight Loss for Given Condition (50 Hrs, 700°F)

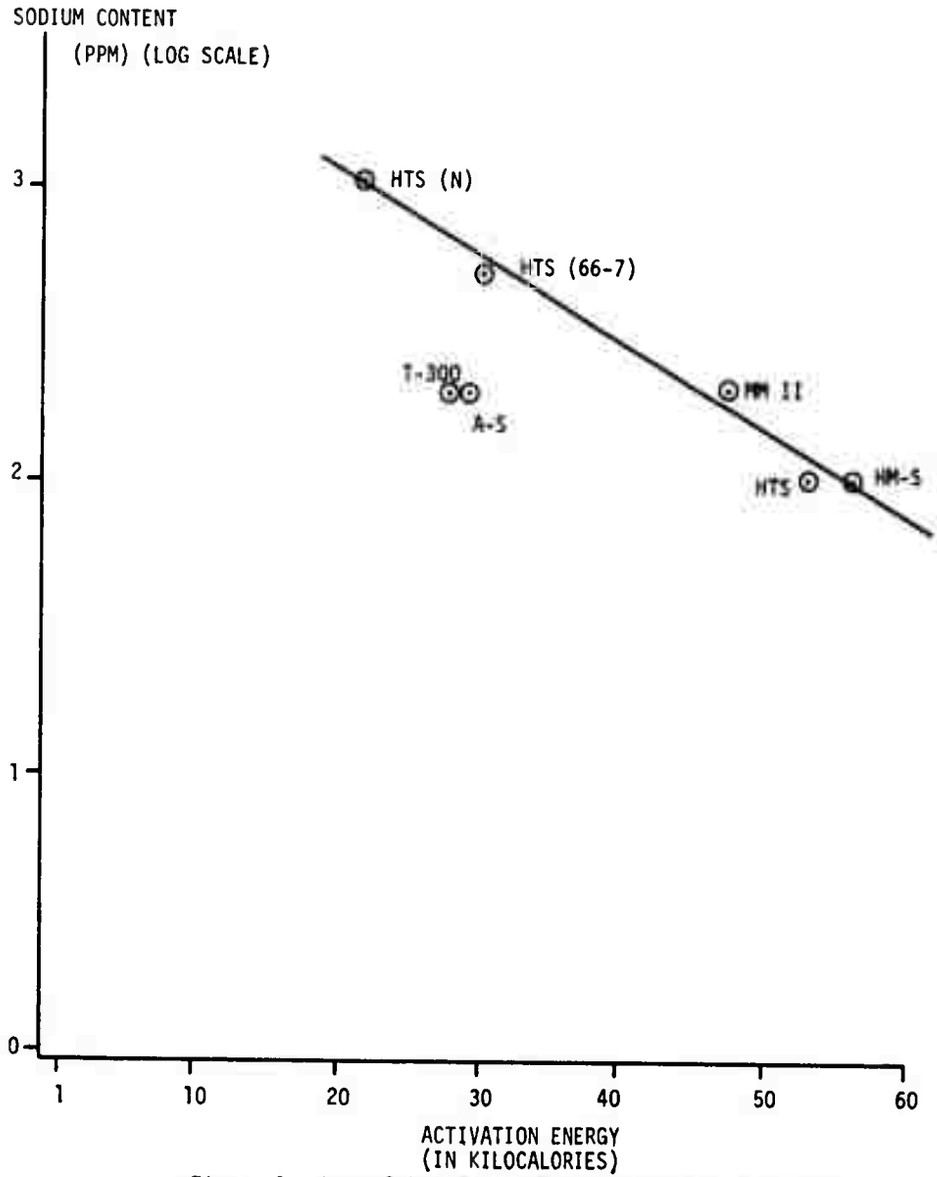


Figure 3. Log of Sodium Content vs. Activation Energy

Energies of activation were then calculated from the Arrhenius equation using the data for the 700°F ITWL study only. These values of E are shown in Table 8.

TABLE 8

ACTIVATION ENERGIES

Fiber Grade	E (activation energy in kilo calories)
HM-S	57
HTS(O)	53.6
MMII	48
A-S	29.9
T-300	29.0
HTS(N)	22.9
HTS(66-7)	30.6

An analysis was made of the effect of sodium content on activation energy. This relationship is illustrated in Figure 4. This graph indicates that sodium concentration lowers the activation energy for isothermal weight loss of graphite fibers.

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

The graphite fibers available today have distinct maximum temperature ranges where they retain maximum performance levels. Great Lakes' CG-5 and Hercules' HM-S for example are stable at very high temperature conditions (700°-800°F). Modmor II and some batches of Hercules' HT-S also have stability at high temperatures. Celion 6000 and Thornel 300 HP (high purity) have stability at the more moderate elevated temperatures (600°-700°F). Hercules' A-S and Union Carbide's T-300 have maximum thermal-oxidative stability at intermediate temperatures (400°-600°F). Several batches of Hercules' HT-S however were found to have poorer stability than other HT-S batches. Lastly, Great Lakes' CG-3, whose surface was untreated, had inferior stability compared to the other fibers.

The presence of the element sodium on or in the fibers appears to have a direct relation to the thermal-oxidative degradation of graphite fibers. The fiber CG-3 is a good example. Apparently this untreated fiber retained a large amount of sodium. It is not known whether sodium is the cause or an indicator of a certain reaction mechanism. Sodium could act as a catalyst to speed up the oxidation of graphite. It is recommended that fiber manufacturers take steps to reduce the concentration of sodium in their product intended for high temperature applications to improve fiber thermal-oxidative stability.

Additional future research should be directed toward the thermal-oxidative stability of graphite-reinforced composites. The surface effect of thermally aging graphite must not be underestimated. Other researchers (Reference 1) have found thermal aging affects the surface sufficiently to reduce the composite interlaminar shear strength.

This work was not directed at ranking the products of fiber producers. Its purpose was to define optimum performance temperature ranges where the fibers still retain significant stability. It was also desirable to determine those parameters (e.g., residual trace elements) that significantly alter elevated temperature performance or stability.

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